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Microscopic Description of Bond Strength Mechanisms and Processes

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Abstract
What we are going to try doing today is look inside some polymeric materials and see what happens on this scale. We are going to look at rather selected polymeric materials since this is the state of the art as we have developed it at this time. I hope at least that it will give you some insight as to what happens on the inside of materials in general. I think as engineers that we have to be interested in this.

Disciplines
Materials Science and Engineering | Structures and Materials

MICROSCOPIC DESCRIPTION OF BOND STRENGTH MECHANISMS AND PROCESSES

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Gentlemen, it is a pleasure for me to be here today to talk to you. I would like, particularly, to thank Dr. Thompson for inviting me and Dr. Kaelble for recommending that he invite me.

The talk that I am going to be giving is going to be a rather different talk than what you have heard in the past. The bonds that I talk about are going to be related to, but once again, very different from the adhesive bonds which you will hear about later today.

What we are going to try doing today is look inside some polymeric materials and see what happens on this scale. We are going to look at rather selected polymeric materials since this is the state of the art as we have developed it at this time. I hope at least that it will give you some insight as to what happens on the inside of materials in general. I think as engineers that we have to be interested in this. Normally we treat materials as a continuum, but we should never lose sight of the fact that they are not a continuum, that materials themselves, as we are going to see in today's discussion, are composites. Chemically they may be one material, but physically they are all very much composites, and some of the same types of approaches that are used in composites can help us understand behavior of single composite systems. I think it is only with an understanding of atomic behavior that we can hope to extrapolate to new circumstances where we can see what effect varying parameters may have, and perhaps even help design tests and so forth so we can obtain the most possible information from the fewest tests. For example, we need design tests that may be conducted in a few hours or days to predict behavior for years of service.

Figure 1 is one man's conception of what an oriented polymeric fiber might look like on an atomic scale. This might be something nylon, polyethylene, PET or other semicrystalline material. As you can see, it has a sort of sandwich structure. This so-called semi-crystalline polymer has crystalline regions separated by less oriented regions. In face, it is these regions where the failure occurs, and if we are going to modify the properties of these materials, these are the regions which the material scientists would have to try to modify.

Now, if we try to envision how such a structure might fail, we can see at least two mechanisms. One of them is by bond rupture, in which case one would expect the flaw to advance through the less ordered regions. The other would be an unfolding, or unravelling, of the structure. A commonly used analogy of polymer is a bundle of spaghetti. Failure of this bundle might occur either by the accumulated fracture of the individual pieces of spaghetti or by pulling them out of the matrix.

The question as to how much of each of these two mechanisms takes place in the material is of some importance, and recently, analytical equipment has become available that can help with this determination. One of these is an EPR Spectrometer. EPR stands for electron paramagnetic resonance, sometimes called ESR, for electron spin resonance. Basically, it is a device that can measure the presence of unpaired electrons. Now, since materials such as the polymers are covalently bonded, when you break the bond, the result is two unpaired electrons. So, if you rupture a polymer for example, and if the unravelling was the primary mechanism, going back to that analogy I gave you a few minutes ago of the spaghetti, then you would expect to see little or nothing in the EPR spectrometer. On the other hand, if the primary mechanism was primary bond rupture, then you would expect to see free radicals (unpaired electrons).

The free radical signal or EPR spectra of nylon 6 at various applied loads is shown in Fig. 2. As we increase the load to about 60 per cent of the final ultimate stress for this particular material, we discover that we

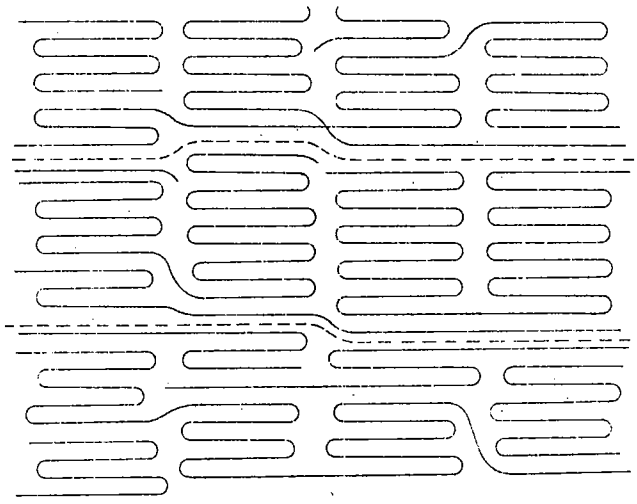


Fig. 1. Morphological model of an oriented fiber proposed by Peterlin

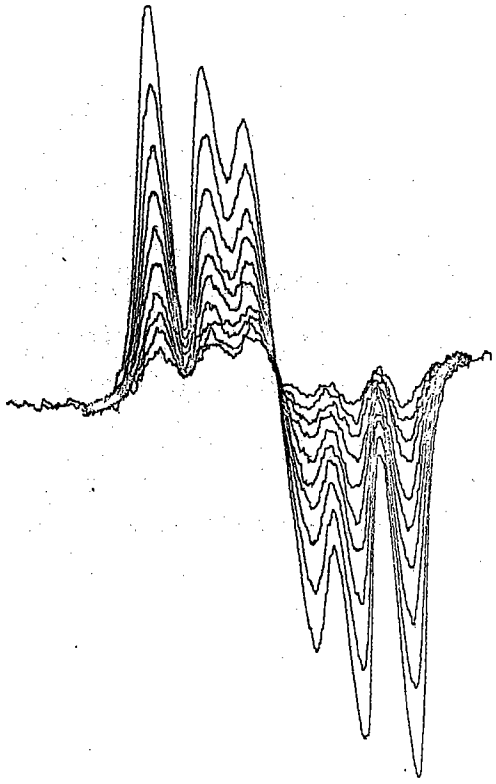


Fig. 2. Growth of EPR spectra during stepwise loading of drawn fibers

start getting a spectra. This indicates that we are breaking primary bonds. These bonds accumulate in larger and larger numbers as the load is increased, as indicated in Fig. 2. Ultimate failure in this case occurred at about 130 ksi. The mode of failure may differ for different polymers and/or testing conditions, e.g. temperature.

For example, in Fig. 3 we have three polymers, nylon, polypropylene, polyethylene. These were fractured at various temperatures which we have normalized here with respect to the Tg, and as you can see in this particular case, below the Tg, the dominate mechanism is apparently bond-rupture. You get large numbers of free radicals in this region representing large concentrations of broken bonds. In fact, the number is in excess of ten to the thirteenth per square centimeter. As you go through the glass transition temperature, the mechanism of failure in these particular materials changes to that of unfolding rather than primary bond rupture. Above this temperature, secondary bond rupture starts to dominate until you get somewhere in the neighborhood of the melting temperature where no detectable bonds are broken.

Now, one of the problems, of course, that the engineer or the scientist is faced with in using materials is the prediction of failure. Many of the more prevalent or more common models of bond rupture relates to a Tobolsky-Eyring type relationship. In these theories, the rate of bond rupture is given by a stress-aided, activation energy of the form $C_B = C_o e - (\frac{U-\sigma\beta}{KT})$. Zhurkov, a rather famous polymer scientist in the USSR, took this equation and proposed that the rate of bond rupture for a constant temperature, at least, ought to be just exponential in the stress.

Zhurkov was the first to do EPR studies of polymer fracture. He found that he was indeed able to get good agreement between his theory and EPR experiments when he increased the stress at a constant rate. We were able to duplicate these Zhurkov studies but when we looked at other loading

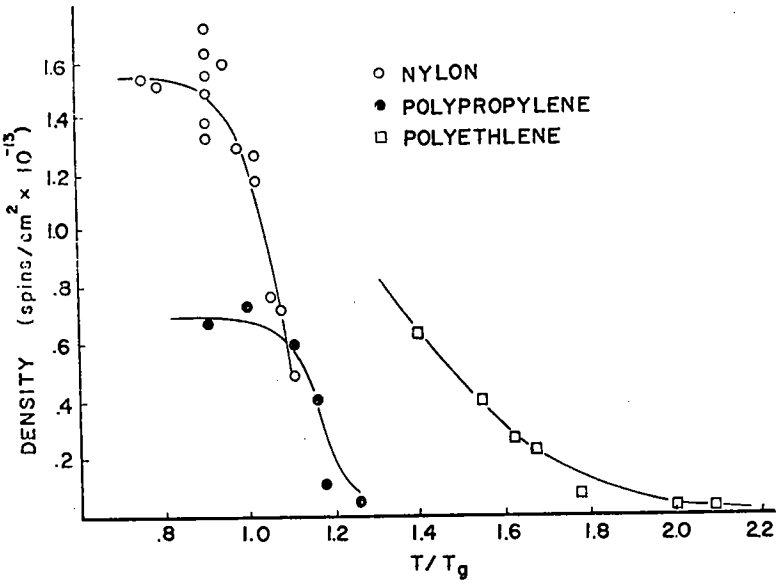


Fig. 3. Free radicals per unit area versus temperature of slicing for various polymers

(e.g. creep) we could no longer fit his model. For instance, we investigated the same relationship when the stress is held constant. In the case of constant stress according to his model the rate of bond rupture ought to be a constant. We found that for such tests the rate of bond rupture was not constant. I don't think it is too hard to see the reason for this failure by referring to the morphology shown in Fig. 1. Note particularly that the tie chains would not all be equally stressed. Referring again to the Zhurkov equation, we note that even if you apply a constant stress to a sample, the stress on the bonds is not constant. It is not the average stress in the material but the local stress on each and every individual bond that is going to result in their rupture. To see that the stress is not constant one might picture this behavior as being something like the behavior of a bundle of strings. One might envision this bundle as having the distribution such that as you pull the strings, all of the strings are uniformly loaded, and then the strength of the bundle is essentially that of all of the strings added together. If N is the number of strings, then the strength is N times the number of strings.

On the other hand, you could have the distribution so broad that as you load the sample, what happens is that each string is loaded and broken independently, and then the strength of the bundle is that of an individual string, although you may have a very large energy absorption in the process. Between these two extremes there are, of course, many possibilities. In each case, one would expect as the bundle is loaded that the more highly stressed strings would fracture first. The cross load would subsequently be redistributed among the remaining strings. Our tests indicate that polymers behave in basically the same way. That is, if the stresses are fairly but not completely uniformly distributed throughout the material, all the bonds are equally stretched, and you get histograms something like those shown in Fig. 4. To construct these histograms an increment of strain is applied to the sample and the number of bonds that are broken is measured. Then another increment of strain is applied and the number of bonds that

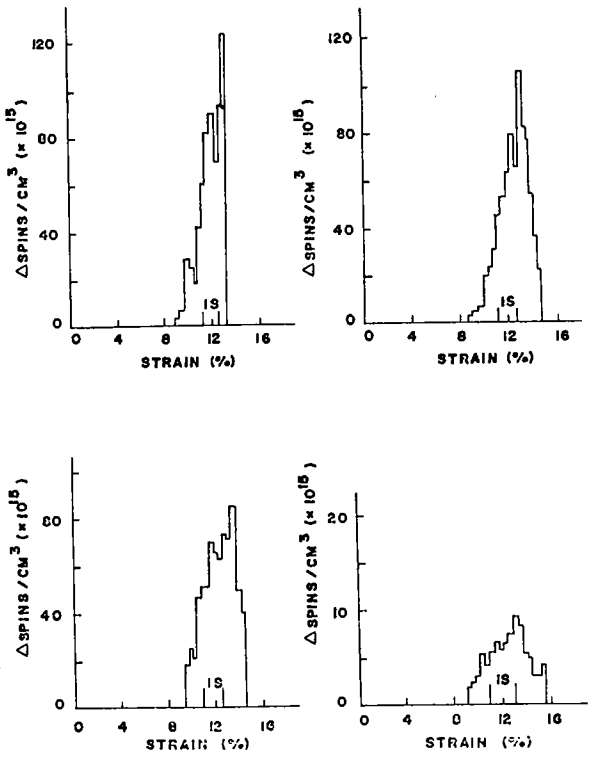


Fig. 4. Histograms of nylon 6 under varying conditions

are broken is measured, etc. For the polymers studied most extensively, the total number of chains broken at fracture remains essentially the same and the fiber strength appears to be mainly a function of the width of these histograms. In fact, we set up a model on the computer where we kept tract of not only the average stress but also the stress on all the different chains in the structure. We thereby obtained the distribution from these histograms from which the behavior could be predicted very accurately. Experimentally we found that the distribution was essentially normal or Gaussian in nature.

Nylon fibers from various manufacturers or after various treatments can have very different strengths. Experimentally, the strength of the fiber versus width of distribution all fall on the same master curve, as shown in Fig. 5. The conclusion is that if you want to make a very high strength nylon fiber, what you want to do is to subject it to treatments such that you will redistribute the stresses throughout the material as uniformly as possible. This is not terribly dissimilar from the way you would want to design a composite. As you can see from Fig. 5, chemically similar nylon can be modified to have strengths from less than 60,000 psi to almost 200,000 psi simply by varying the internal stress distribution. Chemically, the materials are not altered, simply their "composite nature" is altered and this results in a three-fold increase in strength.

Using this type of model in conjunction with the computer to keep tract of the bond rupture, we now have a criterion that will predict the macroscopic stress-strain and strength behavior. If, for example, we subject the sample to a constant strain rate and/or creep test and measure stress-strain and bond rupture behavior, we can determine the "best fit" model parameters. We can then use these parameters to predict from the model behavior for other types of loading. Previous molecular models of fracture could predict behavior for a given type of loading quite well. The real test, however, is can the model predict, using these same parameters, what will happen for other types of loadings. The answer is, "We think yes, with surprisingly good agreement." For example, Fig. 6 shows

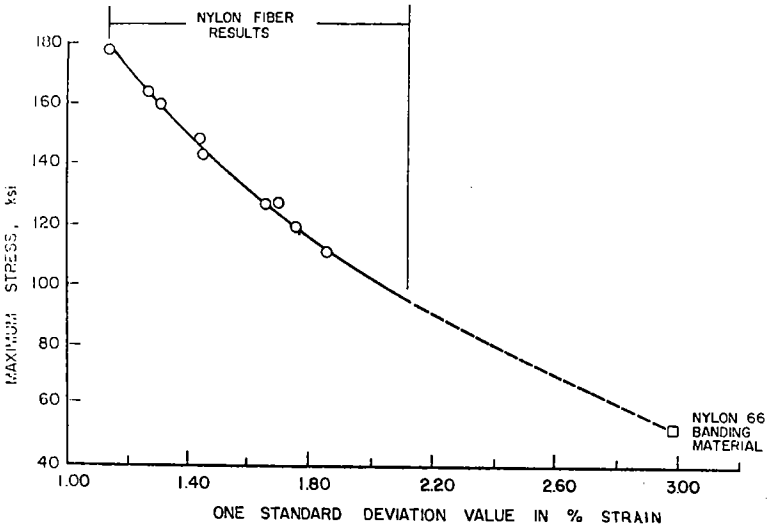


Fig. 5. Max stress to fracture for oriented nylon versus width of histogram

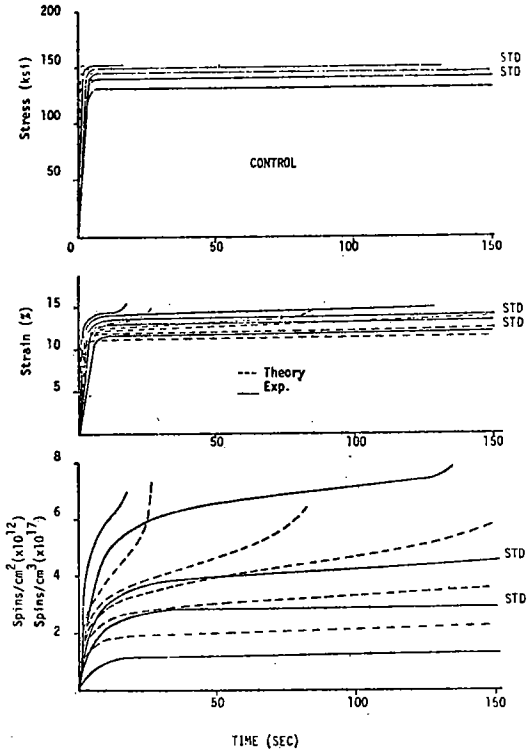


Fig. 6. Comparison of theory with experiment for creep tests of nylon fibers at room temperature

the test that the previous models failed to reproduce, i.e. the creep test. As you can see, agreement between experiment and prediction is as good as you would normally expect to get between two separate experiments. These predictions were obtained using the parameters that were determined from the constant strain rate test. The agreement between experiment and model predictions of what would happen in relaxation tests and low-cycle fatigue tests were equally good. Another pleasing aspect of the model was how well the value of the parameters that the computer said gave the "best fit" with the model compared with the theoretical one or ones obtained from other independent experiments as our best fit. Table I shows a comparison of the ranges found in the literature with the ones obtained here. As you can see, the best fit parameters from the computer model all fail well within the potential limits.

It has also been difficult to predict the effect of temperature on polymer strength. If we look at the effect of temperature on a Tobolsky-Eyring type process, we might view temperature as decreasing the strength of the bond (since it increases the probability of a bond breaking). However, models of polymer fracture that attempt to explain strength purely on this basis generally fail. Our studies indicate that there are two competing mechanisms operating when you change the temperature on a sample. First you have the decrease in the strength of the primary bonds just described but, in addition, the structure is being loosened as well and you are also decreasing the strength of the secondary forces in the material. The strength drops drastically as we increase the temperature, due not only to the weakening of the bonds, but also due to the fact that you are also essentially broadening the distribution in the stress. That is, a given sample loaded at a high temperature will have a broader histogram that the same material loaded at lower temperatures.

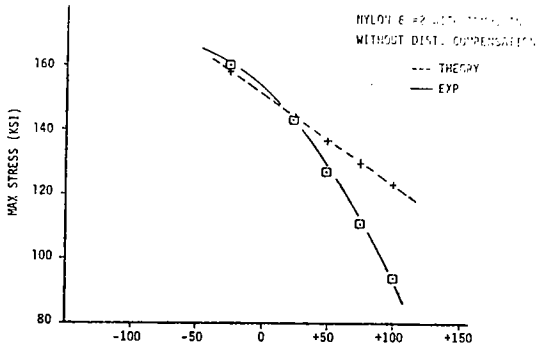
Figure 7 shows these effects. The upper plot, for example, shows what would be predicted for a given case if all you took into consideration was the effect of temperature on primary bond "strength." The lower plot

TABLE I

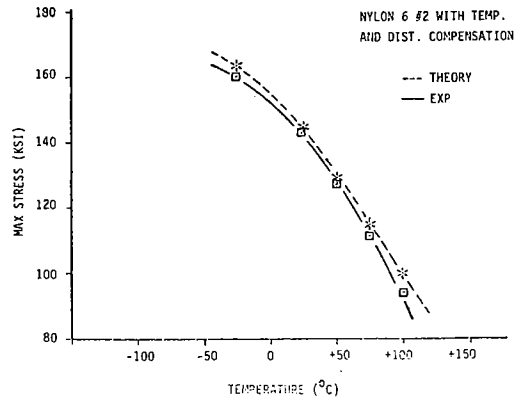
Model Parameters

Parameter	"Best Fit" Value	Theoretical Model Range	Potential Range
S (%strain)	1.25	1.25	no available data
RC	30	20-40	3-50
RL	5	4-10	2-100
$E_b(lb/in^2)$	3×10^7	3×10^7	2.84×10^7
$w_o(sec^{-1})$	10^{13}	10^{13}	$10^{12} - 10^{13}$
U_o $(\frac{Kcal}{mole})$	67.5	65 - 75	43 - 82
γ (A^{o3})	5	3 - 15	1 - 300
$W^*(\frac{chains}{cm^2})$	1×10^{13}	$0.5 - 2.5 \times 10^{13}$	$1 \times 10^{11} - 5 \times 10^{14}$

*arbitrary in theoretical model



a.



b.

Fig. 7. (a) Solid line shows experiment effect of temperature on fracture stress. Dashed line is model predictions where the effect of structure loosening is neglected.
(b) Same as above except dashed line is for model which includes structural loosening effects.

takes into consideration both this temperature change and the temperature widening of the distribution. Here the agreement with experiment is quite good. Note that no new parameters have been introduced, use is made only of the experimentally determined broadening of the histograms and the previously determined parameters.

Having an understanding now of the fundamental mechanism provides us with a tool. Figure 8 shows the results of some work done by Dr. Statton and June Park in our laboratory. In this work samples are "stretch annealed." What is done in this case is to apply either a positive or negative stretch to the sample (negative is defined as leaving slack in the sample) and then raise the temperature. Those chains that are in the structure that are most taut now are under high stress. When you increase the temperature, these highly stressed chains can pull partly out of the surrounding structure, and as a consequence the stress is more uniformly distributed in the sample. This may result in a rather attractive enhancement in the subsequent strength of the material by some 30 per cent for the stretch anneal material or a decrease for the slack annealed fibers.

A similar study and analysis can reveal the difference in behavior of polyethylene and nylon. Chemically, nylon is just polyethylene with an amide group placed periodically, the exact position depending on the particular type of nylon. If polymer strength depends solely (or largely) on strength of the polymer chain, one would, at first glance, expect polyethylene to be stronger (or at least as strong) as nylon. After all a chain is no stronger than its weakest link, and all we have done to make nylon is add an amide link to the polyethylene chain. However, experience tells us otherwise and conventional nylon fibers are, in general, stronger than polyethylene fibers. We would attribute this effect to the very wide histograms that we have experimentally observed for polyethylene fibers, resulting in a proportionately reduced strength. We feel this also explains the observed very high strength and modulus of extended chain poly-

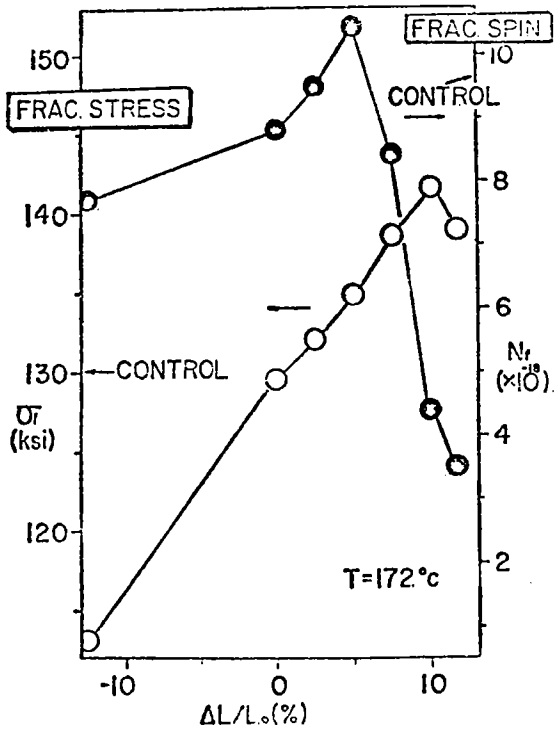


Fig. 8. Fracture stress and free radical concentration at fracture as a function of stretch annealing

ethylene produced by Porter at Boston College and Ward in England. This extended chain polyethylene reportedly has strength and moduli approaching that of steel.

Well, so much for the fibers. I thought I would talk also a little bit about some of the other polymer systems we have studied with EPR. You are all aware, I am sure, that rubbers very often have various fillers added to them. One of the things that happens as a consequence of adding these fillers is that you drastically modify the mechanical properties. You can, for example, introduce other modes of possible failure, i.e. dewetting of the filler. To study this mechanism, to see how much bond rupture was taking place in rubbers and the means by which the mechanical properties might be improved, we undertook this study. Initially three fillers were studied, i.e. (1) glass beads, (2) NaCl and (3) HiSil. The first was chosen because glass beads are known to have very little adhesion to the matrix material. We chose the sodium chloride because it is reported to have sort of an intermediate adhesive property, and finally activated quartz HiSil 233 was chosen because it is thought to have extremely high adhesive forces between the matrix and the filler.

The EPR studies had to be done at low temperatures because the free radicals that are produced in rubber are unstable at or above room temperature. Most of the studies were made at -50° C or lower.

Under these conditions where there is good adhesion between the filler and the ribber matrix strong signals are developed as you pull the sample. This is not true of all substances. For example, glass beads do not have good adhesion and no EPR signal is developed at all. On the other hand, when sodium chloride is used as a filler moderate EPR signals are produced and very strong signals are developed in the case of a HiSil filler. This is demonstrated in Fig. 9.

It is interesting to correlate these results with electron micrographs of the filled material. Typical photomicrographs are shown in Figs. 10, 11 and 12. It will be noted that almost complete dewetting of

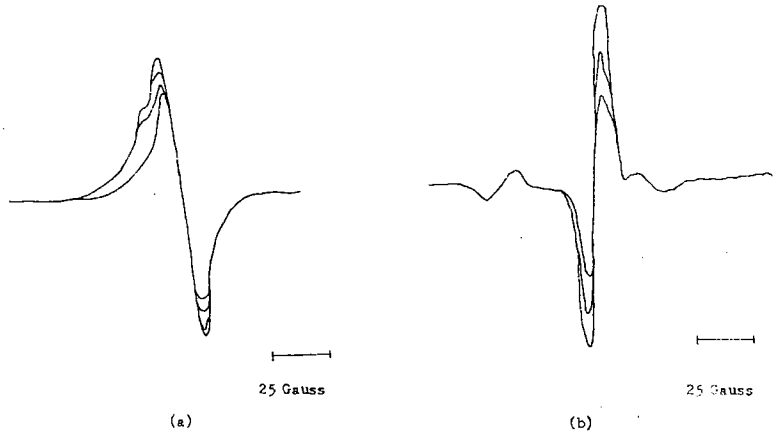


Fig. 9. EPR spectra for residual and stretched
(a) HiL Sil-filled polyisoprene
(b) NaCl-filled polyisoprene

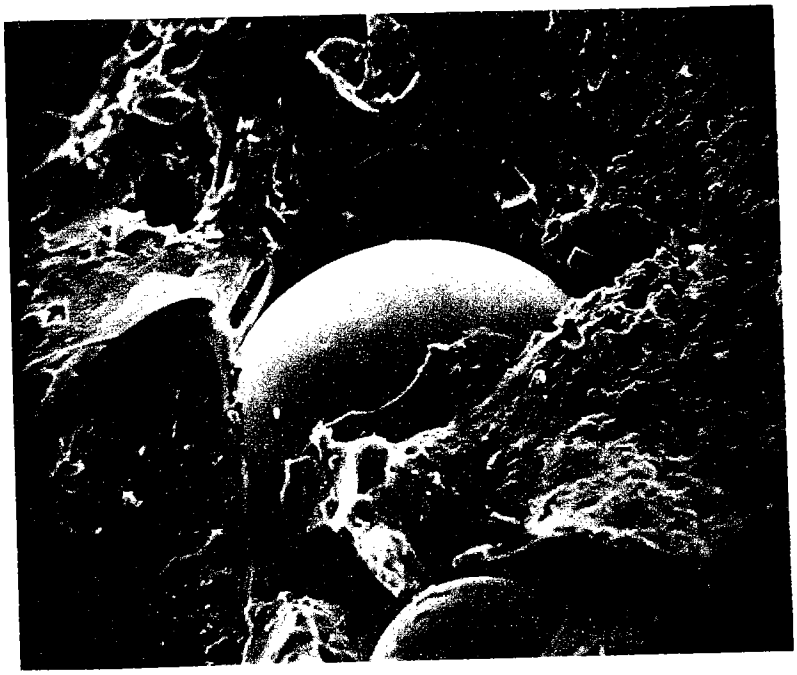


Fig. 10. Dewetting of glass filled EPDM subjected to 30% elongation magnified 130x

Fig. 11. Dewetting in NaCl filled rubbers subjected to 100% elongation mangified 150x

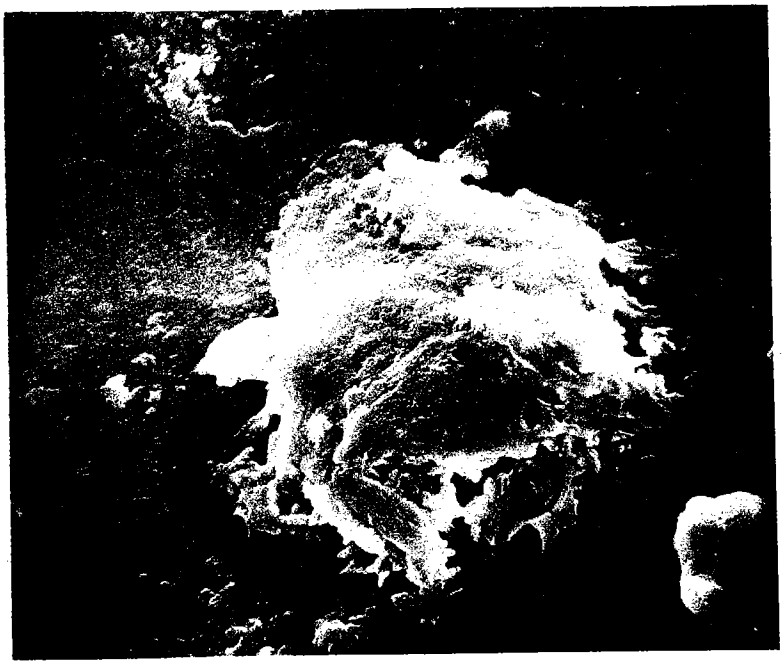


Fig. 12. Hi Sil filled rubber sample subjected to 200% elongation magnified 600x

the glass occurs at 30 percent elongation. The same thing is true of sodium chloride, but if you examine these photos closely, you see evidence of some of the rubber being pulled loose by the sodium chloride. It is also noteworthy that we had to get up to a hundred percent elongation before we started seeing this dewetting behavior. Figure 12 shows the behavior of HiSil at 200 pecent elongation, and you can see no evidence at all of the rubber matrix having pulled away from it.

Tables II and III list the number of free radicals per particle, and per square centimeter of particle surface. We are currently studying toughness of these rubbers and correlating toughness to the data of this table and there seems to be a direct correspondence.

Figures 13, 14, and 15 are micrographs of the fracture surfaces for materials with the three fillers. Once again the drastic difference in behavior of the materials is obvious. The glass beads are lying free in the voids or vacuoles with no sign of adhesion. This material has low toughness with the glass acting as a nonreinforcing filler. Figure 14 is a fracture surface for the NaCl crystals at about approximately the same magnification. You will notice that NaCl, too, has pulled away, but at much larger loads, and closer examination reveals considerable evidence of part of the material having been pulled with the filler. Next is a fracture surface of HiSil showing one of the particles (Fig. 15). You can see it is still completely covered with the rubber and it is not surprising that this material is very strong and tough.

Currently, we are extending the study by treating glass beads with various types of Silane and other coupling agents. We are using EPR and systematic treatments to obtain optimum toughness and strength. There is some evidence that if you have things adhere too well, the sample may be less tough than where some dewetting occurs. Apparently partial dewetting can contribute to the energy dissipation in the sample.

In the final few minutes of this presentation I would like to turn to another rubber sample material. EPR has proven to be a sensitive tool for investigating ozone attack on rubber. Ozone is known to have a very detrimental effect on rubber. Much of the cracking that occurs in rubber parts is attributed to ozone that is in the atmosphere.

TABLE II. Spin-Filler Data at Failure for NaCl-Filled* Polyisoprene**

Type of Test and Values of the Parameters Being Held Constant	Parameter Being Varied and the Value for Each Test	At Failure				
		Stress 10^2 psi	Strain %	#Spins/ cm^3 $x10^{14}$	#Spins/ particle $x10^5$	#Spins/ cm^3 of filler surface $x10^{11}$
Constant Strain Rate 0% Prestrain Varying Temperature	Temperatures -102°C	10.5	1.7	21.0	1.3	3.3
	- 95°C	19.5	2.9	27.5	1.53	3.9
2.15×10^{-3} in/sec	- 75°C	26.0	3.9	15.5	0.618	1.6
Constant Temperature 0% Prestrain Varying Strain Rate	Strain Rate 7.05×10^{-4} in/sec	23.5	1.4	16.0	0.983	2.5
-102°C 0% Prestrain	5.0×10^{-4} in/sec	16.5	1.1	10.5	0.907	2.3
	*2.4×10^{-4} in/sec	31.5	3.0	18.5	1.17	3.0
Constant Temperature and Strain Rate Varying Prestrain	Prestrain 50%	20.0	1.8	3.0	0.250	0.64
	100%	21.0	1.7	10.0	0.438	1.1
	150%	26.5	3.6	5.0	0.265	0.68

*Was still in ductile state and did not fail. Data given at point where test was terminated

**200-300 NaCl crystals in the amount of 50% by weight

TABLE III. Spin-Filler at Failure for Hi-Sil-Filled Polyisoprene**

Type of Test and Values of the Parameters Being Held Constant	Parameter Being Varied and the Value for Each Test	At Failure				
		Stress $\times 10^2$ psi	Elongation %	#Spins/cm^3 $\times 10^{14}$	#Spins/particle $\times 10^5$	#Spins/cm^3 of filler surface $\times 10^{11}$
Constant Strain Rate 0% Prestrain Varying Temperature 2.15×10^{-3} in/sec 0% Prestrain	Temperatures -102°C	28.9	2.2	86.0	4.08	0.2
	- 95°C	21.2	3.2	58.0	3.0	7.69
	- 75°C	1.9	16.0	7.5	2.95	7.56
Constant Temperature 0% Prestrain Varying Strain Rate -102°C 0% Prestrain	Strain Rate 2.15×10^{-3} in/sec	21.9	2.2	86.0	4.08	10.2
	7.04×10^{-4} in/sec	20.8	2.2	11.5	1.96	5.02
	*5.0×10^{-4} in/sec	17.5	11.0	10.0	1.99	5.10
Constant Temperature and Strain Rate Varying Prestrain -95°C 2.15×10^{-3} in/sec	Prestrain 50%	43.0	3.0	66.0	12.0	30.8
	100%	35.0	3.0	65.0	11.6	28.7
	150%	37.0	5.6	20.5	3.49	8.95

*Still in ductile state and did not fail. Value was taken at point where test was terminated

**HiSil 233 58.5 parts by weight

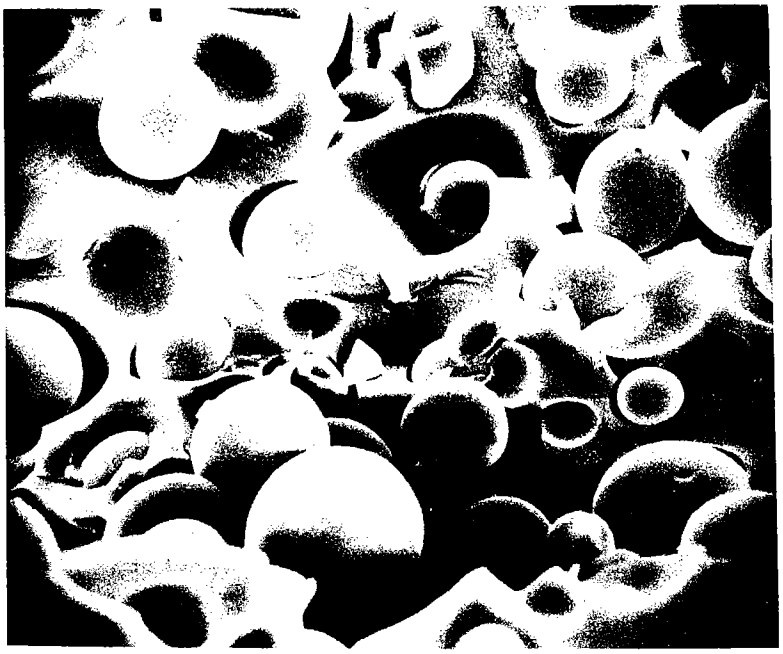


Fig. 13. Fracture surface of glass filled rubber fractured at -102°C magnified 575x

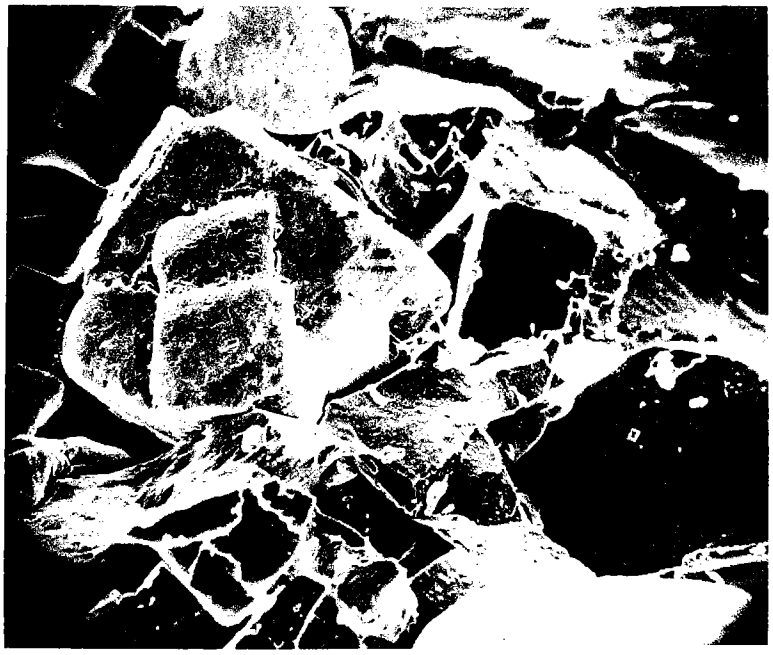


Fig. 14. Fracture surface of NaCl filled rubber fractured at -102°C magnified 120x

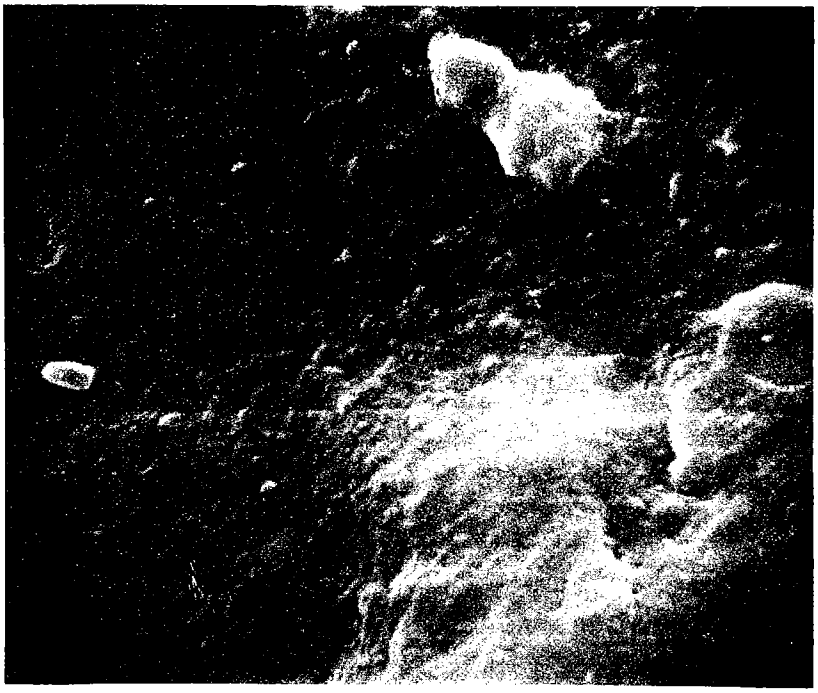


Fig. 15. Fracture surface of HiSil filled rubber fractured at 102°C magnified 1000x

Figure 16 gives some idea of the sensitivity of EPR in detecting ozone damage. The uppermost spectra signal here represents something like 10^{17} free radicals in the cavity. The Varian E-3 EPR spectrometer has a sensitivity of approximately 10^{12} for signals of this width. We are, therefore, approximately five orders of magnitude above threshold sensitivity. In fact, we would find that we would get very strong EPR signals for loaded rubber at stress levels, ozone concentrations and times that were several times less than where we could see any visible sign of damage to the sample using the electron microscope or optical microscopes. So, EPR is a very sensitive tool.

Tests were conducted by building up the equilibrium ozone concentration. The load was next applied to the sample. (It is generally assumed that ozone will not attack unstretched rubber.) If the applied stress exceeds a threshold, then it is accompanied by a rapid increase in free radical concentration and an apparent decrease in sample stiffness as the stress-ozone crack proceeds. In the rubber studied most extensively (B. F. Goodrich Hycar 1043) the threshold is about 13 per cent. For other rubbers such as natural rubber, it might be as low as 4 per cent. In each rubber studied, however, ozone itself is not sufficient to break the bonds. It must have this aiding by the applied stress.

The number of bonds that are broken is experimentally found to increase linearly with strain. See Figs. 17 and 18. These tests were conducted at 2.8 milligrams per liter ozone concentration. We have shown, however, by using other ozone concentrations that it is linear in the ozone concentrations as well. Below 13 per cent strain there is no rapid ozone induced bond rupture for this particular rubber which happens to be B. F. Goodrich Hycar 1043 an acrylonitrile butadiene rubber.

We have been able to make some rather interesting correlations between bond rupture and classical fracture mechanics. Griffith was the first to postulate that a useful fracture criteria could be developed from the hypothesis that the energy required to create a fracture surface came from

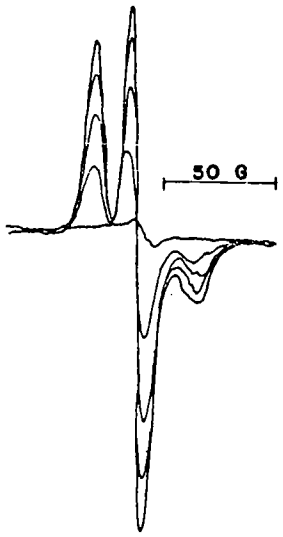


Fig. 16. EPR residual and ozone-stress degraded Hycar 1043 rubber

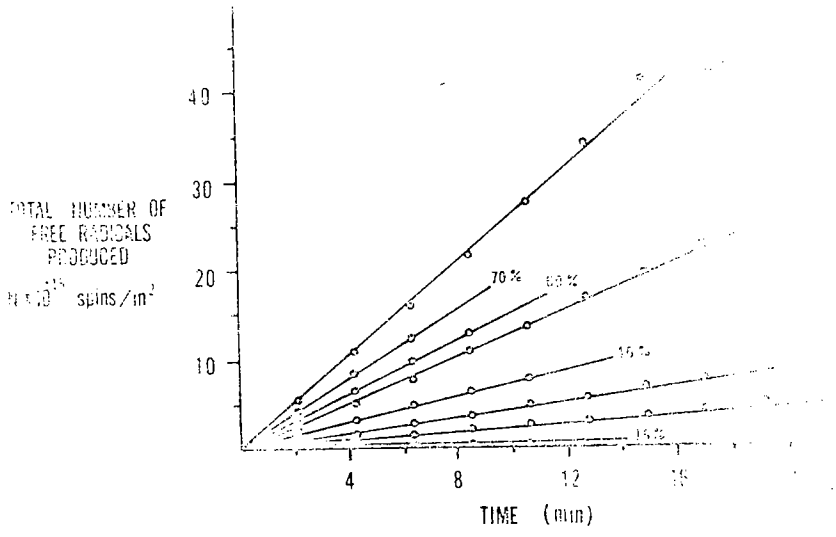


Fig. 17. Total number of free radicals produced vs. time at various strains for Hycar 1043 rubber (2.8 mg/liter ozone concentration)

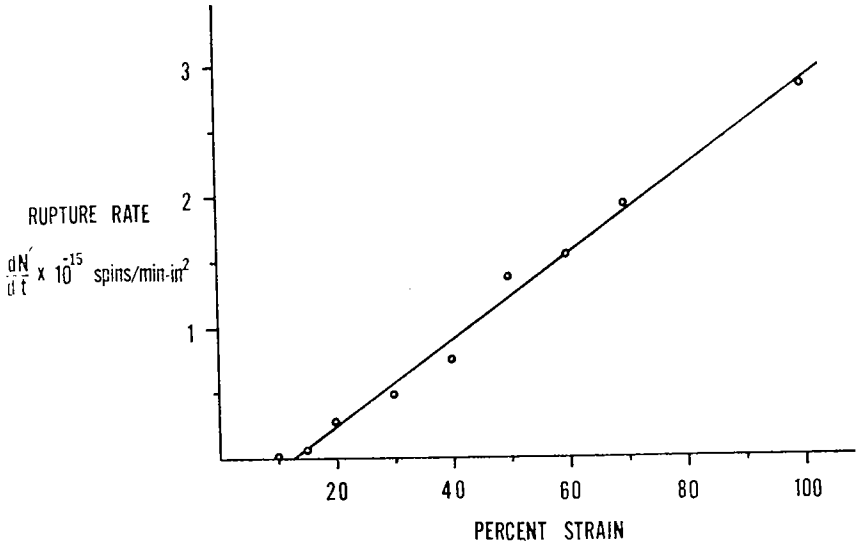


Fig. 18. Slopes from Fig. 17 vs. strain

the strain energy density, γ, times the rate of increase in surface energy to the strain energy release rate due to the crack growth. Griffith treated this as a macroscopic phenomena and investigation of the growth of macro-cracks.

Analogously, we may look at it on an atomic scale. Here rather than the rate of "creation" of crack area we speak of the rate of bond rupture. One can convert from this model to Griffith's by multiplying the energy to break a bond by the number of ruptured bonds required to create a unit of fracture surface. For an ideal isotropic rubber this conversion factor would be approximately 2×10^{14} broken bonds/cm^2.

Looking at it very schematically using a relaxation test, we apply a displacement to a sample, maintain the sample at a fixed stretch ratio and then admit ozone to the system. If we are above the threshold strain of 13 per cent, bonds will start breaking. The energy required for chain scission can come from the stored strain energy in the same as well as chemical energy provided by interaction with the ozone. Since both ozone and strain energy need to be present in order to rupture the bonds, part of the energy must come from both sources.

In this study, analogous to classical mechanics, a standard test is used to determine the specific fracture energy, γ, (energy required from the strain field to rupture a bond). The thermodynamic energy balance is particularly simple for the relaxation (constant displacement) test. For our purpose, we will, therefore, take this as our standard test. Once γ is determined from a relaxation test it can be used in the thermodynamic energy balance to predict "rate of cracking" for stress relaxation or other displacements. Excellent agreement between such prediction and experiments were obtained for relaxation tests.

Now, the real question is: Can we, using γ from this particular test, predict what will happen for other types of loading? The answer is yes. Excellent agreement was obtained for creep and fatigue (cyclic

strains) tests. In fact for all the tests studied predictions from the thermodynamic energy balance and experimental results differed by less than $\pm$ 12 per cent. Figure 19, for example, shows the results.

Tests have also been conducted on samples exposed to torsional stresses. Once again the thermodynamic energy balance using the γ determined from the tensile relaxation tests gave accurate predictions of torsional stress relaxation and the bond rupture kinetics.

In summary we feel EPR is a very valuable tool for looking at the fundamental mechanisms that are taking place. As far as trying to tie into this conference, all of our testing has been destructive rather than non-destructive. It should, however, be possible to devise non-destructive techniques using this tool. For example, it should be possible to use the technique to locate the threshold for bond rupture (i.e. the point at which permanent damage occurs) in fibers used in composites. It could also be used to determine the strain threshold at which ozone attack occurs in rubbers. Measurable free radical concentrations are produced before serious damage results.

Thank you for your attention.

The authors would like to acknowledge the support of the National Science Foundation that made portions of this study possible. We also acknowledge the assistance of several graduate students in accumulating and integrating the data.

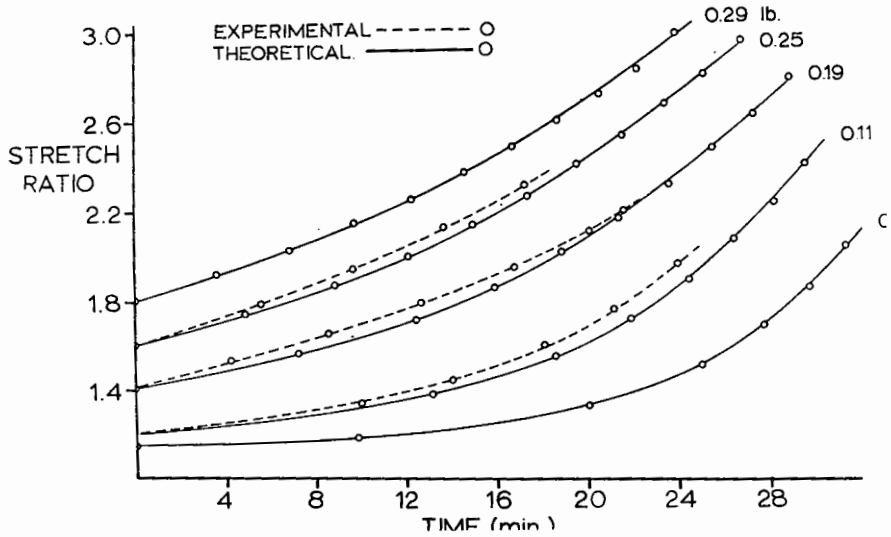


Fig. 19. Comparison of theory and experiment for ozone-stress creep in Hycar 1043

DISCUSSION

DR. ANTHONY EVANS (National Bureau of Standards): Those fracture energies which you were using for your correlation, were they obtained by inference or by direction measure?

DR. DeVRIES (University of Utah): In the latter study?

DR. EVANS: Yes, from the latter study.

DR. DeVRIES: They were determined from direct measurement in relaxation tests. The experimentally measured γ turned out to be something like about half of the total energy to break the bond. We theorize that the reason ozone does not break the bond itself is because half of the energy has to come from the stress field. This is also why there is a threshold strain below which you do not rupture the bonds other than those residually stressed ones.

DR. EVANS: How does that energy compare with what you say you were using in the fracture mechanics specimen?

DR. DeVRIES: If you take the γ per bond and multiply by the theoretical number of bonds per unit area you obtain a specific fracture energy roughly 1.5 to 3 times that obtained from more classical experiments. Now, I would interpret this as saying the crack finds paths of least resistance through the material. It can apparently find paths that require only about 1/2 to 1/3 as many bonds be ruptured if it went through an average path.

DR. DON THOMPSON (Science Center, Rockwell International): Do these bonds recover on a one-to-one basis?

DR. DeVRIES: You mean when you unload the sample?

DR. THOMPSON: Yes.

DR. DeVRIES: No, they don't. We and others have made several studies of this effect. Eventually they do react with other free radicals or impurities and disappear. In fact, you have to be very careful in your choice of polymers to study. In many polymers these reactions occur very rapidly. We chose systems and conditions that maximized the free radical life times. We attempted to make careful measurements of the free radical decay kinetics so that we could extrapolate to zero time. In nylon, for example, at room temperature in the absence of O_2 the free radical half life is something over two hours. You, therefore, have plenty of time to conduct the tests. If you want to run tests longer than two hours and have a knowledge of the decay kinetics, you can extrapolate to obtain the net bond rupture.

DR. GERALD GARDNER (Southwest Research Institute): I want to follow that up. I realize my question is going to be naive, but when the bonds break, presumably as long as they remain broken the material is weaker. It won't sustain as great a stress as it would without that.

DR. DeVRIES: Right.

DR. GARDNER: I gather from the answer to a previous question that these free radicals are chemically very active--

DR. EVANS: Right.

DR. GARDNER: Presumably, they disappear by forming or reforming covalent bonds.

DR. DeVRIES: Right.

DR. GARDNER: Does the material regain its mechanical strength?

DR. DeVRIES: Very little; very little indeed. Look (holding the tip of two fingers on each hand together), we have two bonds here that break. These two spring up and these two spring down. Now, there are four free radicals. The chances of those getting back down here and con-

necting on here are much less, many, many times less than their chance of combining with adjacent free radicals. This, of cource, results in little load-carrying capability in the initial load direction.

Does that answer your question?

DR. GARDNER: Yes. So it doesn't regain its strength because essentially it just forms loops?

DR. EVANS: Right.

DR. GARDNER: Rather than strands of bonds.

Now, this means if I brought you a piece of material and handed it to you and said, "Stretch it and see how many bonds will break", you wouldn't exactly know how strong it is from that measurement?

DR. DeVRIES: No, I wouldn't. Nylon that has a strength of 50,000 psi and nylon that has a strength of 180,000 have essentially the same number of bonds crossing a unit area. It is just that the stress is distributed differently among these.

DR. GARDNER: Well, what it is that I am trying to grasp, is how you could tell from a measurement of the density or the occurrence of detectable free radicals what the load-carrying ability of the piece of material is?

DR. DeVRIES: Okay, I have to have two things. First, I have to know the number of bonds, N, let's call it, and in addition, I have to know how N is distributed. That is the purpose of these histograms that I showed earlier.

DR. GARDNER: Distributed with respect to what now?

DR. DeVRIES: Pardon?

DR. GARDNER: Distributed with respect to what?

DR. DeVRIES: With respect to strain is what we have plotted down here, and over here then is the ΔN. It is just a histogram then. As you load it down, coming back to this analogy again, if all of them are uniformly loaded it is like taking a handful of strings that are all exactly the same length. I pull on it and the strength of the bundle is N times the strength of the individual string. On the other hand, if some of them are very long and some very short-in fact, take the extreme case where I have got ten strings and there is an inch difference in the length of all of them, and they will pull a half inch before they break. Now, as I pull the bundle, I break the first string. I go another half inch and I break another string. I go another half inch, and I break another string. Even though the strength of the bundle is just the strength of the individual strings, I now have gotten a very large elongation before all of them fail. The energy absorbed may also be drastically different.